

polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ^{13}C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

Conversions of Liquefaction

The structures of low-rank coals are characterized by smaller aromatic ring clusters joined by a higher proportion of weak crosslinks than coals of higher rank. This kind of structural feature results in their thermally sensitive natures. The bond cleavages of those weak crosslinks may occur at low temperatures to yield free radicals. If the radicals are not stabilized, retrogressive reactions producing materials difficult to liquefy will take place. Therefore, it is important to determine the optimum temperatures for each coal at which thermal cleavages readily occur while retrogressive reactions are unlikely to occur. Liquefaction experiments were carried out at 250°C, 300°C, 350°C, 400°C and 450°C with the presence of H_2 and the absence of a catalyst and a solvent. The conversion data are shown in Figure 1. At 350°C and below, reactions of all three coals are very limited, with conversions below 20%. As temperature increases to 400°C and 450°C, conversions significantly and continuously increase. However, our earlier study [8] has shown that although a temperature of 450°C seems to be more beneficial in obtaining high conversions, it causes severe retrogressive reactions which are indicated by very high aromaticities of the reaction residues. Therefore 400°C is considered to be the best temperature for liquefaction of these coals.

However, even at the optimum temperature, 400°C, no more than 50% of the coals can be converted to THF solubles when neither a catalyst nor a solvent is involved. In an effort to enhance the conversions, ATTM was added as a catalyst precursor; tetralin and 1-methylnaphthalene were used as a hydrogen donor and a non-donor solvent respectively. The effects of the catalyst and solvents are presented in Figure 2. By using the catalyst, the conversions were increased from 45% to 95.5% for the DECS-1 coal, from 24.2% to 78.5% for the DECS-9 coal, and from 30.6% to 63.5% for the DECS-11 coal. These increases are contributed by significant gains in oils and asphaltenes. The gas yields in the catalytic and non-catalytic reactions are very similar for each coal, which is in an agreement with our earlier observation that the gas yield is a function of temperature, and the use of the catalyst or the donor solvent has no significant effect on it [8]. To maximize the conversion, tetralin and 1-MN were applied in addition to the catalyst. As a donor solvent, tetralin further causes more coal converted to THF solubles for DECS-9 and DECS-11. For DECS-1, there is no increase in conversion, although that is because even with only the catalyst, the conversion reaches 95%. It is reasonable to say that this may already be the practical maximum conversion limit. As a non-donor solvent, 1-MN has a very insignificant effect on the conversions of all the three coals. Comparing conversions at different reaction conditions, it is found that adding the catalyst is sufficient to achieve the highest conversion for the DECS-1 coal; while it is necessary to add both the catalyst and the donor solvent for the DECS-9 and the DECS-11 coals. Among these coals, the DECS-11 is relatively unreactive, its conversion can reach only about 80% at the best reaction condition applied in this study.

Product Characterization

To produce materials from a coal for making the special chemicals, a high conversion has to be achieved and, more importantly, those desirable structural units in the coal macromolecular network have to be converted to individual molecules. In this work, one- to four-ring aromatic or alkylaromatic compounds were desired. In other words, more aromatic carbons have to be converted to THF solubles. To determine the amounts of aromatic carbons converted, the reaction residues as well as the vacuum-dried coal samples were analyzed by CPMAS ^{13}C NMR. The spectra were curve-fitted and integrated, and the aromaticities (f_a) were calculated based on the areas covered by the spectra in aromatic and aliphatic regions. Since the weights of both coals and residues are known, and data of overall conversions from coals to THF solubles are available, the percentages of the reacted aliphatic and aromatic carbons can be determined, as shown in Figure 3 and 4. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed, while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the least. In Figure 4, the aromatic carbons appear to be more difficult to be removed from the coal networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with. This indicates the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the

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DECS-1 coal, the catalyst is sufficient to achieve over 95% aromatic conversion; for the DECS-9 coal, with both the catalyst and the donor solvent, 98% can be obtained; while for the DECS-11 coal, the least convertible coal in terms of conversion, even with both the catalyst and the donor solvent, only about 70% aromatic conversion can be achieved.

The asphaltenes and the preasphaltenes were also studied by CPMAS ^{13}C NMR. Unfortunately, their spectra look so much like the vacuum-dried coals that they can not be characterized without other analytical techniques. The hexane solubles, defined as oils, were analyzed by gas chromatography, identified by gas chromatography/mass spectrometry. Figure 5 represents the oils from the DECS-9 coal without the catalyst or the donor solvent, *a*; with the catalyst but not the donor solvent, *b*; and with both the catalyst and the donor solvent, *c*. In Figure 5-*a*, the oil contains a high proportion of long-chain alkanes, i. e. from $n\text{-C}_{12}$ to $n\text{-C}_{33}$. At retention time of about 6.0 minutes, there is a very strong peak identified as toluene. In low-rank coals such as DECS-9, small aromatic clusters dominate [4, 5], and they are connected by aliphatic crosslinks. Once the crosslinks break, these small aromatic clusters will be released. In the DECS-9, as shown in our recent work [4], one-ring structural units are abundant and thus when liquefying the coal, toluene (instead of benzene) will be a major product, because the benzylic C-C bond has a much lower dissociation energy than the phenyl C-C bond [9]. Relative to those of aliphatics, the amounts of aromatic compounds in the oil (with relation times from 15 minutes to 30 minutes) are much smaller (Figure 5*a*), indicating that this reaction condition suppresses the production of aromatic compounds in the oil. Comparing with the case without the catalyst or the donor solvent, adding ATTM into the reaction system appears to favor the yields of aromatic compounds. As shown in Figure 5*b*, the alkylbenzenes, phenol and alkylphenols are the major components in the oil. This observation agrees with our earlier finding that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons [8]. Furthermore, when we use tetralin in addition to the catalyst, the yields of phenolic compounds remain very high, Figure 5*c*; the one-ring aromatics seem to be in a lower proportion; and the yields of two-ring aromatics, such as indane, alkylindanes and alkyl-naphthalenes have increased. The large peaks at retention times about 24.5 minutes and 27.0 minutes are due to tetralin and naphthalene, the solvent and the dehydrogenated solvent. It is likely that the increased yields of alkylindanes and alkyl-naphthalenes are due, at least in part, to the use of tetralin. In the GC study, three- or four-ring compounds appear to be in small amounts and not affected by either the catalyst nor the solvent. This may be because they are less abundant than the one- or two-rings in the coal, or because their solubilities in hexane are smaller and therefore it is hard to detect the differences at different cases.

CONCLUSIONS

In liquefaction of the three low-rank coals, temperature is found to be optimum at 400°C. Reactions without the catalyst or the donor solvent provide very low conversion, i. e. less than 50%, for all three coals. As for the DECS-1 coal, the ATTM-derived catalyst is sufficient in terms of a high conversion. As for the DECS-9 coal, only when both the catalyst and the donor solvent are used can conversion as high as 98% be achieved. For the DECS-11 coal, even under the best reaction condition, which is at 400°C with the catalyst and the solvent, the conversion only reaches 78%. Therefore, the DECS-11 coal is the least convertible coal among the three.

The investigation on reaction residues by solid-state NMR shows that it is relatively easier to convert aliphatic carbons from coals to THF solubles, and that the catalyst and the donor solvent can both be beneficial but the effects are moderate. The amounts of aromatic carbons being converted from the coals appear to be small when the catalyst or the donor solvent is not present, and they can even be negative, indicating that retrogressive reactions have occurred. Adding the catalyst and the solvent significantly enhances the reactions of aromatic carbons.

The study of the oils agrees with what has been observed on the residues. Without the presence of the catalyst or the solvent, the oils contain large amounts of long-chain alkanes; while with the catalyst and the donor solvent, more aromatic materials, such as phenolic compounds, alkylbenzenes and some two-ring compounds, can be produced. With further extraction and purification, these compounds might be used as for making specialty chemicals for some advanced materials.

ACKNOWLEDGEMENT

The authors gratefully thank the United States Department of Energy for the financial support. We also want to thank Dr. M. Baird and Dr. M. A. Nowak for helpful discussions.

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Table 1. Analysis of the coal samples

	DECS-1	DECS-11	DECS-9
Sources & Rank			
state	Texas	North Dakota	Montana
county	Freestone	Mercer	Bighorn
city	Fairfield		Decker
seam	Bottom	Beulah	Dietz
ASTM rank	subbit C	lignite	subbit B
sampling date	12/11/89	6/15/93	6/12/90
Proximate (wt%, ar)			
moisture	30.0	33.4	24.7
ash	11.1	6.4	4.8
volatile	33.2	37.4	33.5
fixed carbon	25.8	22.9	37.1
Elemental (wt%, dmmf)			
carbon	76.1	74.2	76.1
hydrogen	5.5	4.4	5.1
nitrogen	1.5	1.0	0.9
organic sulfur	1.1	0.4	0.3
oxygen	15.8	20.0	17.5

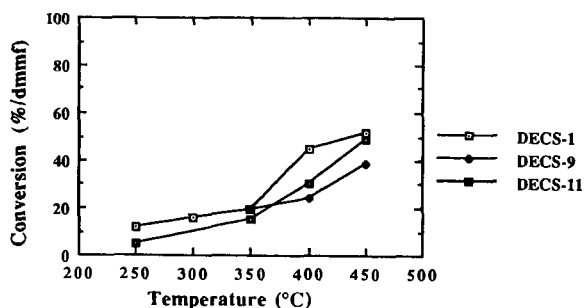


Figure 1. Conversions of the three coals at temperatures from 250°C to 450°C without a catalyst or a solvent

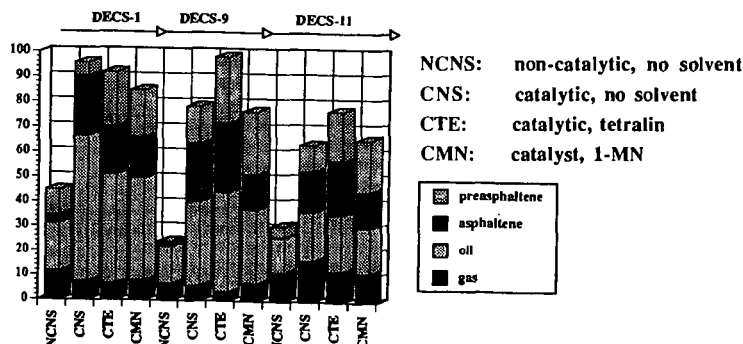


Figure 2. Liquefaction conversions of the three coals at 400°C under four different reaction conditions

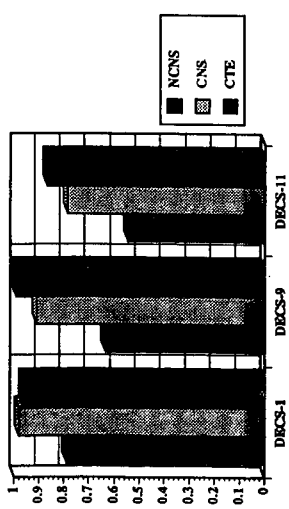


Figure 3. The amounts of aliphatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

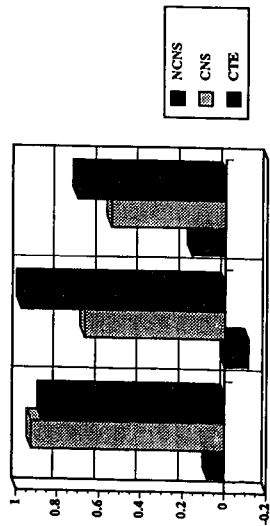


Figure 4. The amounts of aromatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

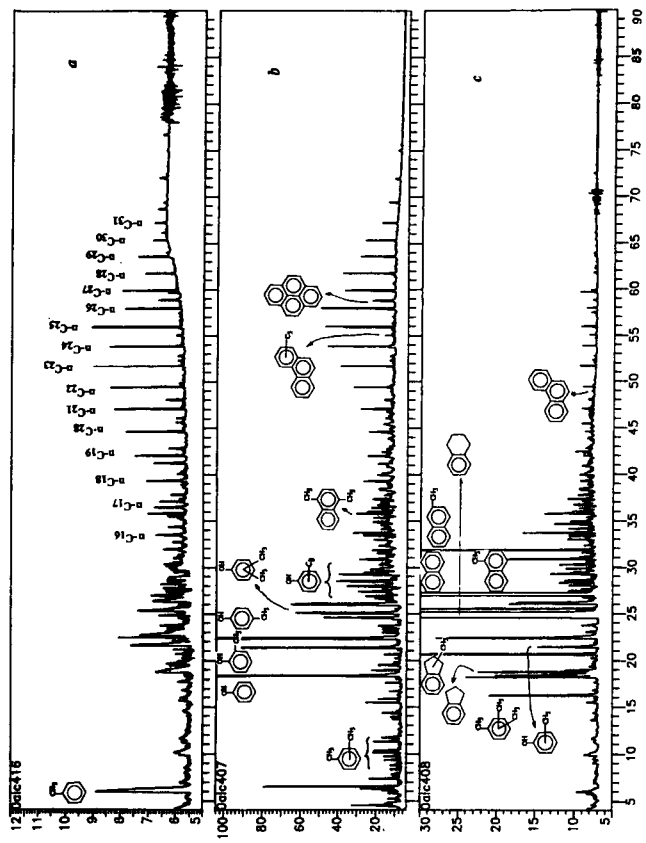


Figure 5. Analysis of the oil samples from the DECS-9 coal using gas chromatograph. a) the sample from the reaction without a catalyst or a solvent; b) the sample from the reaction with the ATTM-derived catalyst but without a solvent; c) the sample from the reaction with both the catalyst and tetralin.